(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 303 957 A1**

# (12) EUROPEAN PATENT APPLICATION

(21) Application number: 88112984.5

(51) Int. Cl.4: C22C 19/05

(22) Date of filing: 10.08.88

(30) Priority: 11.08.87 JP 200577/87
19.01.88 JP 9233/88

(43) Date of publication of application:
22.02.89 Bulletin 89/08

(84) Designated Contracting States:
DE FR GB SE

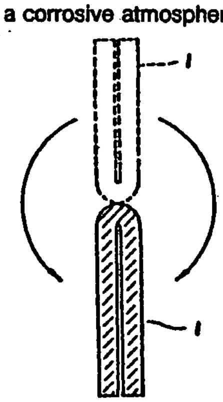
(71) Applicant: MITSUBISHI KINZOKU KABUSHIKI KAISHA
5-2, Ohtemachi 1-chome
Chiyoda-ku Tokyo 100(JP)

(72) Inventor: Takizawa, Yoshio
160-4, Sasayama
Hasuda-City Saitama(JP)
Inventor: Noguchi, Masatoshi
279, Niitsutsumi
Ohmiya-city Saitama(JP)
Inventor: Sekine, Ichiro
11-103, Parktown Wakamiya 1-8, Wakamiya
Okegawa-city Saitama(JP)

(74) Representative: Türk, Gille, Hrabal
Bruckner Strasse 20
D-4000 Düsseldorf 13(DE)

## (54) Corrosion resisting alloy and corrosion resisting member.

(57) A corrosion resisting Ni-base alloy containing 38 to 50 wt% Cr, 0.1 to 2 wt% of at least one of Mo and W, 0 to 2 wt% Cu, 0 to 3 wt% Zr, 0 to 3 wt% Nb, 0 to 3 wt% Ta, 0 to 3 wt% Hf, 0 to 0.01 wt% Ca, 0 to 0.01 wt% of Y and other rare-earth elements, 0 to 0.05 wt% C, and 0 to 0.04 wt% N. The alloy can be subjected to plastic working such as rolling, wire stretching, drawing or the like. The alloy can be used in a dipping equipment such as a dipping bath or a bucket, in agitating members within the dipping bath, and further in pipes, valves, pump components and electrode members used in a corrosive atmosphere.




(c)

Fig. 1

EP 0 303 957 A1

# CORROSION RESISTING ALLOY AND CORROSION RESISTING MEMBER

## BACKGROUND OF THE INVENTION

The present invention relates to a Ni-Cr alloy member having excellent corrosion resistance and excellent bending workability. The alloy member is suitable for constituting a dipping equipment represented by a dipping bath, a dipping jig such as a bucket, an agitating instrument or the like within the dipping bath, and a pipe, a valve, a pump component or the like.

The inventors of this application have found that, because of the corrosion resistance and the excellent workability, the alloy according to the invention is not limited merely to the dipping equipment, but reveals remarkable advantages in application also to, for example, an electrode of an electrolytic polishing apparatus or other electrodes exposed to corrosion atmosphere. The inventors also recognize that the alloy according to the invention is not limited to the above applications, but is epoch-making new one having both corrosion resistance and workability.

Corrosion resisting alloys are known, for example, from U.S. Patent No. 2,777,766 (Hastelloy G), U.S. Patent No. 3,203,792 (Hastelloy C-276), U.S. Patent No. 3,160,500 (Inconel 625), U.S. Patent No. 3,573,901 (Inconel 690) and the like. However, any of these alloys are not sufficient in corrosion resistance. In view of these circumstances, the inventors of this application have developed an alloy improved in corrosion resistance, as disclosed in Japanese Patent Application Laid-Open No. 58-17247. However, the alloy developed by the inventors cannot be said to be superior in plastic workability, and is limited in application to cast material. Further, G.B. Patent No. 1,281,597 has proposed a technique of improvement in mechanical strength of a corrosion resisting alloy formed of a Ni-base alloy high in Cr, exposed to high temperature. The present invention can be said to be a further improvement in a mechanical characteristic of the alloy disclosed in the G.B. patent.

The inventors of this application have developed the alloy improved in corrosion resistance in Japanese Patent Application Laid-Open No. 58-17247. However, uses of the developed alloy are limited only to cast component parts. Accordingly, a conventional corrosion resisting alloy, which is insufficient in corrosion resistance, but is excellent in plastic workability, in particular, in bending workability, has been used for a member for which bending working is required at manufacturing of the member, such as, for example, a dipping equipment represented by a dipping bath, a dipping jig such as a bucket, an agitating instrument or the like within the dipping equipment, and a pipe, a valve, a pump component or the like, as well as an electrode of, for example, an electrolytic polishing apparatus exposed to corrosion atmosphere.

## SUMMARY OF THE INVENTION

The inventors of this application have perceived the fact that when the content of the Cr is brought to 38 to 50 wt%, a Ni-Cr alloy fundamentally maintains a predetermined corrosion resistance while damages such as cracking or the like at working or processing are difficult to occur and, in addition thereto, when a solid soluble range of one or both of Mo and W is 0.1 to 2 wt%, corrosion resistance and plastic workability remarkably coexist within the range.

Cu, together with Cr, Mo and W, has a function of improving corrosion resistance of the alloy. However, the content of Cu exceeding 2% does not reveal a further improvement in effect. Accordingly, the content of Cu is determined to 2% or less.

Further, the inventors of this application have found that double fusion by the use of a vacuum fusion method and an electroslag fusion method makes it possible to bring contents of respective C and N elements serving as unavoidable impurities, to a value equal to or less than 0.05 wt% for C and a value equal to or less than 0.04 wt% for N. In particular, damages of a member represented by "cracking" at working high in degree of processing can remarkably be improved.

Moreover, particular limiting of an amount of Cr to 43 to 47 wt% causes a precipitation amount of the alpha phase of the Cr solid solution to be restrained to a value equal to or less than 10% in area ratio, making it possible to secure the corrosion resistance and the plastic workability at a high level.

Furthermore, Cu, Zr, Nb, Ta and Hf have conventionally been added by 1 to 3% by volume as principal elements, for the purposes of improving corrosion resistance for Cu and workability for Zr, Nb, Ta and Hf. In

this invention, however, C is brought to a value equal to or less than 0.01 wt% and N is brought to a value equal to or less than 0.01 wt%, whereby excellent corrosion resistance and plastic workability can be obtained without addition of the principal elements referred to above.

It has also been known that Y and other rare-earth elements improve the workability of the alloy. In this invention, however, a value equal to or above 0.01 wt% has not revealed further advantages or effects.

Ca has advantageous in deoxidation and desulfurization at dissolution and manufacturing of the alloy. However, if the content of Ca exceeds 0.01 wt%, the alloy is embrittled, so that damages tend to occur in the member after having been worked or processed.

Additionally, other than the elements mentioned above, the Ni-Cr alloy according to the invention contains, as unavoidable impurities, 0.3 wt% or less Fe, 0.3 wt% or less Mn, 0.3 wt% or less Ti, 0.3 wt% Al and 0.05 wt% or less Mg.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1a and 1b are schematic cross-sectional views showing alloy plates which are subjected to bending tests in accordance with JIS;

Fig. 1c is schematic cross-sectional view showing alloy plate which is subjected to an additional bending test performed after the bending test as shown Figs. 1a and 1b;

Fig. 2 is a perspective view of a dipping jig for a dipping equipment, which is a first example formed of an alloy according to an embodiment of the invention;

Fig. 3 is a perspective view of a bucket for the dipping equipment, which is a second element example formed of the alloy;

Fig. 4a is a diagrammatic vertical cross-sectional view of an agitator having incorporated therein an agitating propeller which is a fourth example formed of the alloy;

Fig. 4b is a view similar to Fig. 4a, but showing another aspect of the agitator having incorporated therein the agitating propeller;

Fig. 5a is a perspective view of the electrode formed by the clad member;

Fig. 5b is a view similar to Fig. 5a, but showing another aspect of the electrode formed by the clad member; and

Figs. 6 to 9 are photomicrographs of cross-sections of alloy plates of the present invention, respectively.

## DETAILED DESCRIPTION

Various examples of the alloy according to the invention will be described below.

[Examples]

Firstly, molten metals of the alloy having a required compositions were melted by using a high-frequency vacuum furnace, and cast in dies to form ingot of 60 mm in diameter and 200 mm in length. Subsequently, the ingots were melted again by using device for melting electroslag, and each ingot of 100 mm in diameter having compositions shown in Table 1 was prepared. Each ingot was held at the temperature from 1150 to 1250 °C for 10 hours to be homogenized and then subjected to hot casting and hot rolling at a temperature suitable for starting the hot operations within the range of the above-identified temperature to form a hot rolling plate of 4 mm in thickness. This plate was held at the temperature from 1100 to 1200 °C for 30 minutes to be homogenized and then subjected to cool rolling to form cool rolling plate of 2 mm in thickness. This plate was held at the latter condition to be homogenized, and thereby manufacturing alloy plates 1 to 55 of the present invention, and comparative alloy plates 56 to 67.

Note that each of the comparative alloy plates 56 to 67 had a composition in which the content (represented by.* in Table 1) of any of the components falls outside the range of the present invention.

Metallic structures of the alloy plates 2, 8, 10 and 55 are shown in Figs. 6 to 9, respectively. Each of area ratios of the alpha phase of the Cr solid solution of the alloy plates as shown in Figs. 6 to 9 was measured by instrument for image analysis, that may be sold by Leitz campany in the name of "TAS PLUS". The results are shown as follows:

| | Content of Cr | Area Ratio of Alpha Phase |
|---|---|---|
| Alloy No. 2 | 43% | 1% |
| Alloy No. 8 | 45.6% | 1 to 1.3% |
| Alloy No. 10 | 46.5% | 8% |
| Alloy No. 55 | 49% | 23% |

As seen the results, each of the area ratios of the alpha phase of the Cr solid solution is restrained to a value equal to or less than 10% when the content of Cr of the alloy plate is at equal to or less than 47%.

Subsequently, as for the alloy plates 1 to 55 of the present invention and the comparative alloy plates 56 to 67, their extensions of a tensile test at a room temperature were measured to evaluate their formabilities, especially bending properties. Also, the plates were subjected to a bending test in accordance with JIS or Japanese Industrial Standard, bending them 180° to bring one inner face of each bending plate into contact with the other inner face and thereby detecting whether cracks appear or not on the bent portion of the plates. Then, the plates having no cracks after the bending test were subjected to an additional bending test, by which the plates were bent in the contrary direction to the former bending test to detect whether cracks appear or not on the bent portion.

According to JIS, the former bending test is prescribed as a test that the alloy plate 1 shown in Fig. 1 (a) is bent as shown in Fig. 1 (b) to detect whether cracks appear or not on the bent portion. Also, the latter bending test is prescribed as a severe or hard test that the alloy plate 1 bent by the former bending test is furthermore bent in a direction which is contrary to the bending direction of the former test to detect whether cracks appear or not on the bent portion. As for both the former and latter bending tests, the results are shown in Table 1.

In Table 1, symbol " X " represents a state that cracks are appeared before alloy plates are completely bent and therefore the alloy plates cannot be bent by the former bending test. Symbol " O " represents a state that cracks are not appeared by the former bending test, and that they are appeared by the latter bending test. Symbol "◎" represents a state that cracks are not appeared both the former and latter bending test.

Further, to evaluate corrosion, the alloy plates were held to dip in a mixed acid such as an aqueous solution of 17% $HNO_3$ containing 3% HF at 60°C for 24 hours, and were held to dip in a mixed acid having composition which is contrary to an aqua regia or an aqueous solution of 55% $HNO_3$ containing 8% HCl at 60°C for 240 hours. The contents of the corrosion were measured by performing the dippings, and the results are shown in Table 1.

Member Example 1 (Dipping Jig Example):

A dipping jig shown in Fig. 2 was made of a rolled strip 5 of 3 mm in thick and a rod 6 of 5 mm in diameter made of the alloy of the present invention, which consists of 46 wt% Cr, 1 wt% Mo, 1 wt% Zr, 0.03 wt% C, 0.004 wt% N and the remainder Ni. The thus made dipping jig serves as an exemplified member. Two kinds of typical alloy compositions employed conventionally were set as follows, and were likewise formed respectively into dipping jigs. These two dipping jigs serve respectively as comparative members. Hereinafter, the members corresponding to their respective alloy compositions will be referred respectively to as "exemplified member", "comparative member A" and "comparative member B".

Alloy A:

23 wt% Cr, 7 wt% Mo, 19 wt% Fe, 2 wt% Cu, 1 wt% Ta, 1 wt% Nb, 0.04 wt% C and the remainder Ni

Alloy B:

30 wt% Cr, 10 wt% Fe, 0.03 wt% C and the remainder Ni

These three kinds of dipping jigs were simultaneously dip in an aqueous solution of 20% $HNO_3$ + 3% HF (60°C) for ten days and, thereafter, reduction amounts of the respective dipping jigs due to corrosion were measured. The reduction amount of the comparative member A revealed 0.71 mm/year, and the reduction amount of the comparative member B revealed 0.25 mm/year. However, the reduction amount of the instant exemplified member revealed only 0.05 mm/year.

Member Example 2 (Dipping Jig Example):

Three buckets, each as shown in Fig. 3, were made of respective rolled strips 11 of 3 mm in thick and respective wire materials 12 of 2 mm in diameter formed of respective three alloys the same in composition as the respective dipping jigs described above. The three buckets were dip in the aqueous solution of 20% $HNO_3$ + 3% HF (60°C) for ten days and, thereafter, reductions in weight of the respective buckets were measured. As a result, the weight reduction amount of the comparative member A was 121 g/m$^2$, and the weight reduction amount of the comparative member B was 53 g/m$^2$, whereas the weight reduction amount of the instant exemplified member was 12 g/m$^2$.

Member Example 3 (Dipping Jig Example):

An exemplified member was formed into a pipe of 10 mm in diameter and 1 m in length, by an alloy composition consisting of 44 wt% Cr, 1.5 wt% Mo, 0.02 wt% C, 0.006 wt% N and the remainder Ni. As comparative members, two pipe members each the same in size as the exemplified member were made of respective comparative alloys A and B the same in composition as the dipping jig example. Subsequently, an aqueous solution of 50% $P_2O_5$ (80°C) was recirculated through each of the three members at flow velocity of 30 m/min for 2400 hours. Thereafter, corrosion rates of the respective pipe members were compared with each other in terms of a weight reduction amount.

The weight reduction amount of the comparative pipe A was 512 g/m$^2$, and the weight reduction amount of the comparative pipe B was 174 g/m$^2$, whereas the weight reduction amount of the pipe according to this exemplified member was 61 g/m$^2$.

Member Example 4 (Dipping Equipment Member Example):

As exemplified members, a dipping equipment member (agitating propeller) having its configuration shown in Fig. 4a or 4b was made of strip material 8 or 10 and pipe material 7 or 9 each having an alloy composition consisting of 44 wt% Cr, 1.2 wt% Mo, 0.5 wt% W, 0.007 wt% C, 0.006 wt% N and the remainder Ni. Comparative members A and B were prepared each of which was the same in composition as the aforesaid dipping jig example and each of which was the same in size and configuration as the exemplified member. These two comparative members and the exemplified member were rotated within an aqua regia (25% HCl + 20% $HNO_3$) (60°C) at 120 revolutions per minute. Consumptive amounts of the respective members were compared with each other. As a result, the consumptive amount of the comparative member A was 14 g/m$^2$, and the consumptive amount of the comparative member B was 3.8 g/m$^2$, while the consumptive amount of the instant exemplified member was 0.02 g/m$^2$ even after an elapse of 240 hours.

Member Example 5 (Electrode Member Example):

As an exemplified member, a clad member was made, by a usual method, of an ordinary steel plate 2 or 4 and an alloy plate 1 or 3 having its alloy composition consisting of 44 wt% Cr, 0.8 wt% Mo, 0.005 wt% C, 0.004 wt% N and the remainder Ni. Subsequently, the clad member was formed into an electrode member for an electrolytic bath as shown in Fig. 5a or 5b. For comparison, clad members each made of conventional steel plate and stainless steel plate made of SUS304 in accordance with JIS were formed

respectively into comparative electrode members each having the same size as the instant exemplified member.

The steel plate sections of the respective exemplified member and comparative member were properly sealed. Subsequently, these two members were used respectively as cathodes, and a stainless steel was employed as an anode. Electrolytic polishing was carried out by the use of an electrolytic solution of 30% $HNO_3$ + 2% HCl (50°C) at current density of 20 $A/m^2$. The cathodes were compared in consumptive amount with each other. As a result, the consumptive amount of the comparative electrode member was 1.3 mm after the use for 24 hours, whereas the consumptive amount of the electrode member according to the instant exemplified member was 0.1 mm after the use for 24 hours.

As described above, it is possible for the alloy according to the invention to extremely easily form requisite various kinds of members for which corrosion resistance is required, without substantial anxiety of restriction in workability. In particular, the alloy according to the invention is excellent as a member accompanied with plastic working such as rolling, wire stretching, drawing or the like. The alloy according to the invention is effective in use for a dipping equipment represented by a dipping bath, a dipping jig such as a bucket, an agitating member or the like within the dipping bath, and a pipe, a valve, a pump component or the like, as well as an electrode member employed in corrosion atmosphere.

## Table 1-1

| Run No. | Composition (wt %) Cr | Mo | W | Cu | Ca | Zr | Nb | Ta | Hf | Y | Rare Earth Elements | Impurities C | Impurities N | Ni and the other impurities | Tensile Extension At a Temperature | Existance of Cracks | Corrosion Rate (mm/year) Mixed Acid | Inverse Aqua Regia |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 38.6 | 0.96 | – | – | – | – | – | – | – | – | – | 0.045 | 0.004 | rem. | 65.5 | ◎ | 0.106 | 0.050 |
| 2 | 43.0 | – | 1.83 | – | – | – | – | – | – | – | – | 0.028 | 0.003 | rem. | 60.3 | ◎ | 0.088 | 0.049 |
| 3 | 44.2 | 0.97 | 0.27 | – | – | – | – | – | – | – | – | 0.014 | 0.021 | rem. | 62.6 | ◎ | 0.074 | 0.046 |
| 4 | 40.5 | 0.68 | – | – | – | – | – | – | – | – | – | 0.029 | 0.004 | rem. | 61.6 | ◎ | 0.098 | 0.040 |
| 5 | 45.5 | 0.12 | – | – | – | – | – | – | – | – | – | 0.022 | 0.006 | rem. | 58.5 | ◎ | 0.071 | 0.052 |
| 6 | 42.1 | 0.96 | – | – | – | – | – | – | – | – | – | 0.018 | 0.003 | rem. | 50.8 | ◎ | 0.087 | 0.053 |
| 7 | 44.6 | 1.52 | – | – | – | – | – | – | – | – | – | 0.031 | 0.003 | rem. | 55.6 | ◎ | 0.078 | 0.035 |
| 8 | 45.6 | – | 0.11 | – | – | – | – | – | – | – | – | 0.032 | 0.004 | rem. | 59.2 | ◎ | 0.075 | 0.054 |
| 9 | 44.6 | – | 0.98 | – | – | – | – | – | – | – | – | 0.037 | 0.004 | rem. | 66.1 | ◎ | 0.076 | 0.042 |
| 10 | 46.5 | 1.21 | – | – | – | – | – | – | – | – | – | 0.029 | 0.006 | rem. | 60.4 | ◎ | 0.077 | 0.049 |
| 11 | 44.2 | 0.97 | 0.27 | 1.0 | – | – | – | – | – | – | – | 0.014 | 0.021 | rem. | 62.0 | ◎ | 0.074 | 0.030 |
| 12 | 44.6 | 1.52 | – | 1.5 | – | – | – | – | – | – | – | 0.031 | 0.003 | rem. | 52.3 | ◎ | 0.058 | 0.020 |
| 13 | 44.6 | – | 0.96 | 0.5 | – | – | – | – | – | – | – | 0.037 | 0.004 | rem. | 53.4 | ◎ | 0.068 | 0.037 |
| 14 | 44.2 | 0.97 | 0.27 | – | 0.032 | – | – | – | – | – | – | 0.014 | 0.004 | rem. | 63.6 | ◎ | 0.072 | 0.048 |
| 15 | 44.6 | 1.52 | – | – | 0.005 | – | – | – | – | – | – | 0.031 | 0.003 | rem. | 52.7 | ◎ | 0.075 | 0.038 |
| 16 | 44.6 | – | 0.96 | – | 0.008 | – | – | – | – | – | – | 0.014 | 0.004 | rem. | 69.3 | ◎ | 0.081 | 0.041 |
| 17 | 44.2 | 0.97 | 0.27 | – | – | 3.0 | – | – | – | – | – | 0.014 | 0.004 | rem. | 64.7 | ◎ | 0.083 | 0.051 |
| 18 | 44.6 | 1.52 | – | – | – | – | 0.5 | – | – | – | – | 0.031 | 0.003 | rem. | 57.8 | ◎ | 0.063 | 0.021 |
| 19 | 44.6 | – | 0.96 | – | – | – | – | 0.8 | – | – | – | 0.014 | 0.004 | rem. | 69.3 | ◎ | 0.060 | 0.027 |
| 20 | 45.6 | – | 0.11 | – | – | – | – | – | 1.2 | – | – | 0.032 | 0.004 | rem. | 63.2 | ◎ | 0.075 | 0.041 |

Table 1-2

| Run No. | Composition (wt. %) Cr | Mo | W | Cu | Ca | Zr | Nb | Ta | Hf | Y | Rare Earth Elements | Impurities C | Impurities N | Ni and the other impurities | Tensile Extension At a Temperature | Existance of Cracks | Corrosion Rate (mm/year) Mixed Acid | Corrosion Rate (mm/year) Inverse Aqua Regia |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 45.5 | 0.12 | – | – | – | – | – | – | 1.0 | – | – | 0.022 | 0.008 | rem. | 60.2 | ○ | 0.071 | 0.035 |
| 22 | 43.0 | – | 1.83 | – | – | 2.5 | 0.2 | – | – | – | – | 0.028 | 0.003 | rem. | 63.4 | ○ | 0.077 | 0.041 |
| 23 | 44.2 | 0.97 | 0.27 | – | – | – | – | 1.3 | 1.1 | – | – | 0.014 | 0.004 | rem. | 64.2 | ○ | 0.068 | 0.031 |
| 24 | 44.2 | 0.97 | 0.27 | – | – | 0.1 | 0.15 | 0.13 | 0.15 | – | – | 0.014 | 0.004 | rem. | 65.7 | ○ | 0.061 | 0.026 |
| 25 | 45.5 | 0.12 | – | – | – | – | – | – | – | – | 0.005 | 0.022 | 0.006 | rem. | 63.4 | ○ | 0.078 | 0.054 |
| 26 | 43.0 | – | 1.82 | – | – | – | – | – | – | 0.005 | – | 0.028 | 0.003 | rem. | 64.1 | ○ | 0.077 | 0.046 |
| 27 | 45.0 | – | 0.11 | 1.0 | 0.005 | – | – | – | – | – | – | 0.032 | 0.004 | rem. | 60.3 | ○ | 0.065 | 0.026 |
| 28 | 44.2 | 0.97 | 0.27 | 1.0 | – | 1.5 | – | – | – | – | – | 0.014 | 0.004 | rem. | 63.5 | ○ | 0.081 | 0.025 |
| 29 | 44.8 | 1.52 | – | 1.2 | – | 0.5 | 0.3 | 1.0 | – | – | – | 0.031 | 0.003 | rem. | 60.3 | ○ | 0.051 | 0.030 |
| 30 | 44.8 | – | 0.96 | 0.5 | – | 1.8 | – | – | 1.2 | – | – | 0.014 | 0.004 | rem. | 71.2 | ○ | 0.068 | 0.031 |
| 31 | 44.2 | 0.97 | 0.27 | – | 0.003 | – | 1.8 | – | – | – | – | 0.014 | 0.004 | rem. | 68.8 | ○ | 0.074 | 0.039 |
| 32 | 45.0 | – | 0.11 | – | 0.008 | 0.7 | – | 1.3 | – | – | – | 0.032 | 0.004 | rem. | 64.1 | ○ | 0.080 | 0.039 |
| 33 | 44.2 | 0.97 | 0.27 | – | – | 1.2 | – | – | – | – | 0.003 | 0.014 | 0.004 | rem. | 70.9 | ○ | 0.073 | 0.041 |
| 34 | 44.6 | – | 0.96 | – | – | – | 1.5 | – | – | – | 0.007 | 0.014 | 0.004 | rem. | 74.1 | ○ | 0.058 | 0.034 |
| 35 | 43.0 | – | 1.83 | – | – | – | – | 1.1 | 1.8 | 0.001 | 0.009 | 0.028 | 0.003 | rem. | 67.2 | ○ | 0.064 | 0.033 |
| 36 | 44.2 | 0.97 | 0.27 | 1.7 | 0.001 | 2.3 | 1.8 | – | – | – | – | 0.014 | 0.004 | rem. | 73.1 | ○ | 0.074 | 0.042 |
| 37 | 44.6 | – | 0.96 | 0.8 | 0.004 | – | – | 1.0 | 1.0 | – | – | 0.014 | 0.004 | rem. | 75.2 | ○ | 0.054 | 0.029 |
| 38 | 44.8 | 1.52 | – | 1.5 | 0.005 | 1.5 | – | 1.5 | – | – | – | 0.031 | 0.003 | rem. | 61.4 | ○ | 0.061 | 0.032 |
| 39 | 45.5 | 0.12 | – | 0.7 | 0.005 | – | – | – | – | 0.005 | – | 0.022 | 0.006 | rem. | 60.8 | ○ | 0.054 | 0.034 |

Table 1-3

| Run No. | Composition (wt. %) Cr | Mo | W | Cu | Ca | Zr | Nb | Ta | Hf | Y | Rare Earth Elements | Impurities C | Impurities N | Ni and the other impurities | Tensile Extension At a Temperature | Existance of Cracks | Corrosion Rate (mm/year) /Mixed Acid | Corrosion Rate (mm/year) Inverse Aqua Regia |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 44.2 | 0.97 | 0.27 | 0.1 | 0.002 | – | – | – | – | – | 0.01 | 0.014 | 0.004 | rem. | 63.9 | ◎ | 0.072 | 0.039 |
| 41 | 44.8 | – | 0.98 | 0.6 | – | 2.5 | – | – | – | – | 0.001 | 0.014 | 0.004 | rem. | 66.7 | ◎ | 0.058 | 0.027 |
| 42 | 44.6 | 1.52 | – | 1.8 | – | – | 1.5 | – | 1.3 | – | 0.008 | 0.031 | 0.003 | rem. | 59.7 | ◎ | 0.058 | 0.034 |
| 43 | 43.0 | – | 1.82 | 2.0 | – | 0.8 | – | 0.5 | – | 0.003 | – | 0.028 | 0.003 | rem. | 64.3 | ◎ | 0.065 | 0.025 |
| 44 | 44.2 | 0.97 | 0.27 | – | 0.003 | 1.3 | – | 1.0 | – | – | 0.003 | 0.014 | 0.004 | rem. | 72.3 | ◎ | 0.076 | 0.037 |
| 45 | 44.2 | 0.97 | 0.27 | – | 0.005 | 1.5 | 1.5 | – | – | – | 0.005 | 0.014 | 0.004 | rem. | 73.1 | ◎ | 0.070 | 0.041 |
| 46 | 44.6 | – | 0.90 | – | 0.007 | 0.3 | – | 0.5 | 1.8 | 0.006 | – | 0.014 | 0.004 | rem. | 67.4 | ◎ | 0.062 | 0.036 |
| 47 | 44.6 | 1.52 | 0.30 | 1.0 | 0.005 | 1.0 | – | – | 1.0 | – | 0.006 | 0.014 | 0.004 | rem. | 58.2 | ◎ | 0.059 | 0.043 |
| 48 | 44.2 | 0.97 | 0.27 | 0.3 | 0.008 | 0.5 | 0.3 | 0.3 | 0.3 | 0.001 | 0.007 | 0.014 | 0.004 | rem. | 74.2 | ◎ | 0.063 | 0.034 |
| 49 | 43.0 | – | 1.83 | – | – | – | – | – | – | – | – | 0.005 | 0.002 | rem. | 62.4 | ◎ | 0.055 | 0.038 |
| 50 | 44.6 | 1.52 | – | – | – | – | – | – | – | – | – | 0.003 | 0.004 | rem. | 60.7 | ◎ | 0.038 | 0.034 |
| 51 | 44.6 | – | 0.90 | – | – | – | – | – | – | – | – | 0.002 | 0.003 | rem. | 68.1 | ◎ | 0.036 | 0.025 |
| 52 | 45.8 | – | 0.11 | – | – | – | – | – | – | – | – | 0.001 | 0.002 | rem. | 60.3 | ◎ | 0.033 | 0.029 |
| 53 | 47.5 | 0.95 | – | – | – | – | – | – | – | – | – | 0.028 | 0.005 | rem. | 45.2 | ○ | 0.088 | 0.040 |
| 54 | 48.3 | – | 0.11 | – | – | – | – | – | – | – | – | 0.031 | 0.004 | rem. | 43.1 | ○ | 0.081 | 0.038 |
| 55 | 49.0 | 0.68 | 0.98 | – | – | – | – | – | – | – | – | 0.014 | 0.003 | rem. | 40.3 | ○ | 0.094 | 0.046 |

## Table 1-4

| Run No. | Composition (wt %) Cr | Mo | W | Cu | Ca | Zr | Nb | Ta | Hf | Y | Rare Earth Elements | Impurities C | Impurities N | Ni and the other impurities | Tensile Extension At a Temperature | Existance of Cracks | Corrosion Rate (mm/year) Mixed Acid | Corrosion Rate (mm/year) Inverse Aqua Regia |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 56 | 38.1* | 0.77 | – | – | – | – | – | – | – | – | – | 0.025 | 0.007 | rem. | 67.2 | ◎ | 0.325 | 0.205 |
| 57 | 61.2* | 0.88 | – | – | – | – | – | – | – | – | – | 0.030 | 0.004 | rem. | 19.8 | × | 0.082 | 0.028 |
| 58 | 44.3 | –* | –* | – | – | – | – | – | – | – | – | 0.031 | 0.005 | rem. | 68.2 | ◎ | 0.217 | 0.138 |
| 59 | 46.7 | 2.13* | – | – | – | – | – | – | – | – | – | 0.028 | 0.005 | rem. | 25.3 | × | 0.078 | 0.041 |
| 60 | 44.8 | – | 2.19* | – | – | – | – | – | – | – | – | 0.033 | 0.004 | rem. | 28.3 | × | 0.078 | 0.045 |
| 61 | 46.2 | 1.00 | – | – | – | – | – | – | – | – | – | 0.081* | 0.002 | rem. | 15.2 | × | 0.148 | 0.089 |
| 62 | 45.3 | 0.93 | – | – | – | – | – | – | – | – | – | 0.036 | 0.050* | rem. | 18.4 | × | 0.083 | 0.047 |
| 63 | 45.3 | 0.93 | – | 1.8 | 0.012* | – | – | – | – | – | – | 0.035 | 0.005 | rem. | 38.9 | × | 0.057 | 0.024 |
| 64 | 43.2 | 0.88 | – | – | – | – | – | – | – | – | – | 0.072* | 0.052* | rem. | 17.8 | × | 0.192 | 0.093 |
| 65 | 44.8 | 1.00 | 0.88 | – | 0.013* | – | – | – | – | – | – | 0.031 | 0.004 | rem. | 30.7 | × | 0.072 | 0.041 |
| 66 | 44.2 | 0.97 | 0.27 | 0.3 | 0.008 | 0.5 | 0.3 | 0.3 | 0.3 | 0.001 | 0.007 | 0.07* | 0.003 | rem. | 27.5 | × | 0.082 | 0.043 |
| 67 | 44.2 | 0.97 | 0.27 | 0.3 | 0.008 | 0.5 | 0.3 | 0.3 | 0.3 | 0.001 | 0.005 | 0.035 | 0.05* | rem. | 26.7 | × | 0.058 | 0.045 |

In the above-indicated Table 1-4, each of values marked * is outof the range of the preferred values of the present invention.

In the column "Existence of Cracks" of all of the tables, a mark of X represents a result that cracks are brought into existence on a piece of an alloy when it is bent so as to hold it in halves, a mark of ○ represents a result that cracks are not brought into existence on the piece when it is bent so as to hold it in halves and that cracks are brought into existence when it is bent in a direction and then is extent and is also bent in the inverse direction, and a mark of ◎ represents a result that cracks are not brought into existence on a piece even when it is bent so as to hold in halves and then is extend and is also bent in the inverse direction.

## Claims

1. A corrosion resisting Ni-base alloy containing 38 to 50 wt% Cr, 0.1 to 2 wt% of at least one of Mo and W, 0 to 2 wt% Cu, 0 to 3 wt% Zr, 0 to 3 wt% Nb, 0 to 3 wt% Ta, 0 to 3 wt% Hf, 0 to 0.01 wt% Ca, 0 to 0.01 wt% of Y and/or other rare-earth elements, 0 to 0.05 wt% C, and 0 to 0.04 wt% N.

2. A corrosion resisting Ni-base alloy according to claim 1, wherein Cr is 43 to 47 wt% and has a metallic structure in which an alpha phase of a Cr solid solution is at equal to or less than 10%.

3. A corrosion resisting Ni-base alloy according to claim 1 or 2, containing 0 to 0.01 wt% C and 0 to 0.01 wt% N.

4. A corrosion resisting Ni-base alloy according to claim 1, wherein Cr is 43 to 47 wt% and has a metallic structure in which an alpha phase of a Cr solid solution is at equal to or less than 10%, and wherein the Ni-base alloy contains 0 to 0.01 wt% C and 0 to 0.01 wt% N.

5. A corrosion resisting Ni-alloy according to claim 4, wherein Zr is 0 to 0.01 wt%, Nb is 0 to 0.01 wt%, Ta is 0 to 0.01 wt% and Hf is 0 to 0.01 wt%.

6. A member for a dipping equipment represented by a dipping bath, a dipping jig such as a bucket, an agitating instrument, etc. within the dipping bath, a pipe, a valve, a pump component, etc., wherein said member is formed of the alloy according to claim 1, 2, 3, 4 or 5.

7. An electrode member consisting of the alloy according to claim 1, 2, 3, 4 or 5.

8. Use of the corrosion resisting Ni-base alloys of claim 1, 2, 3, 4 or 5 for the preparation of dipping equipments or electrode members.

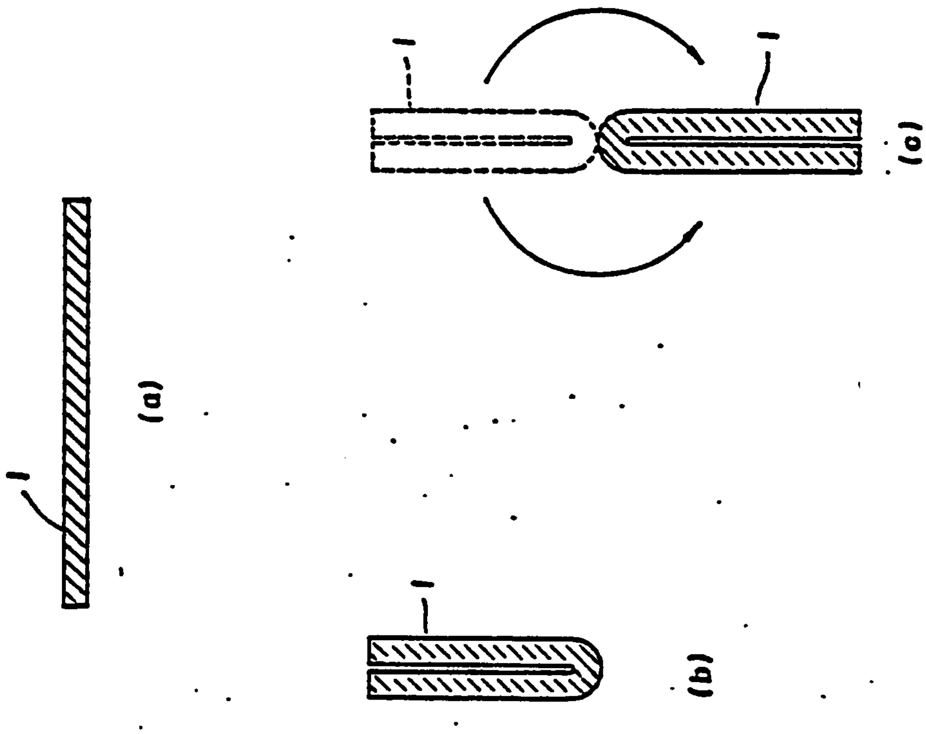



Fig. 1

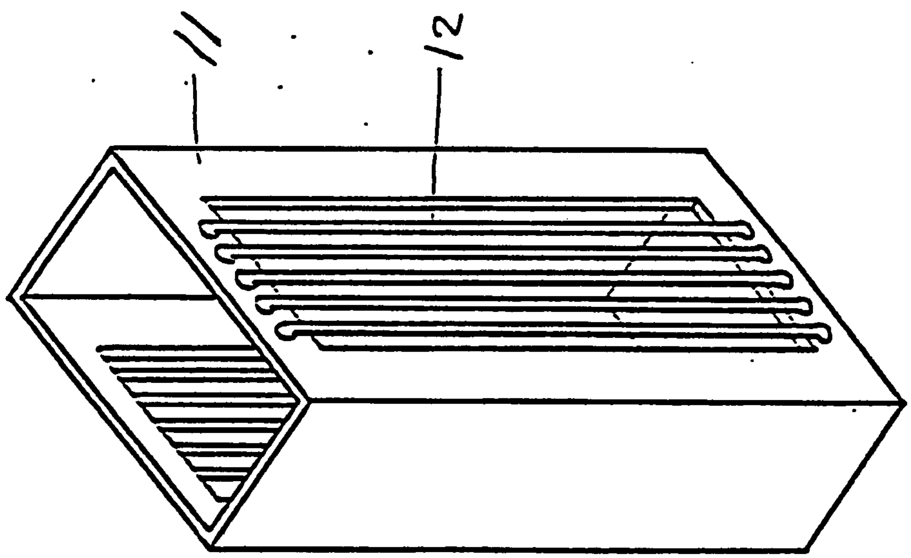



Fig 3

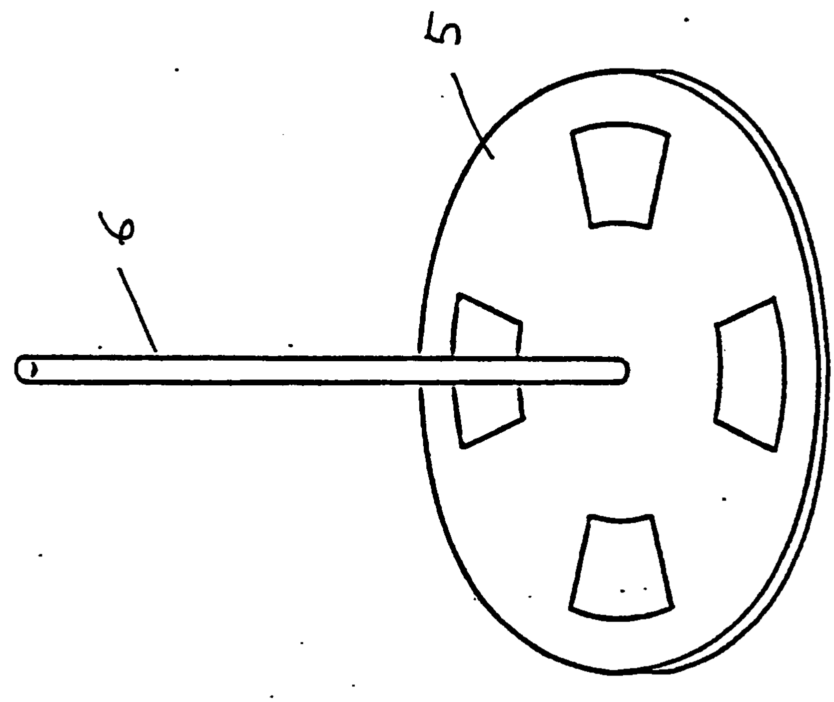



Fig 1

Fig 4a

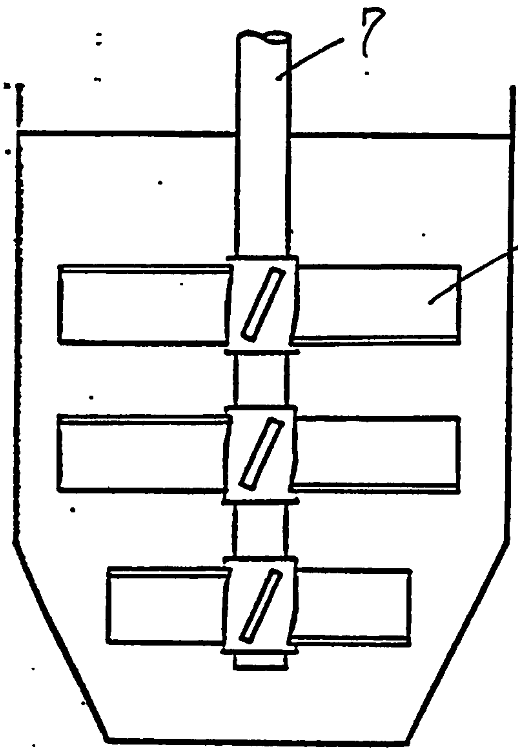
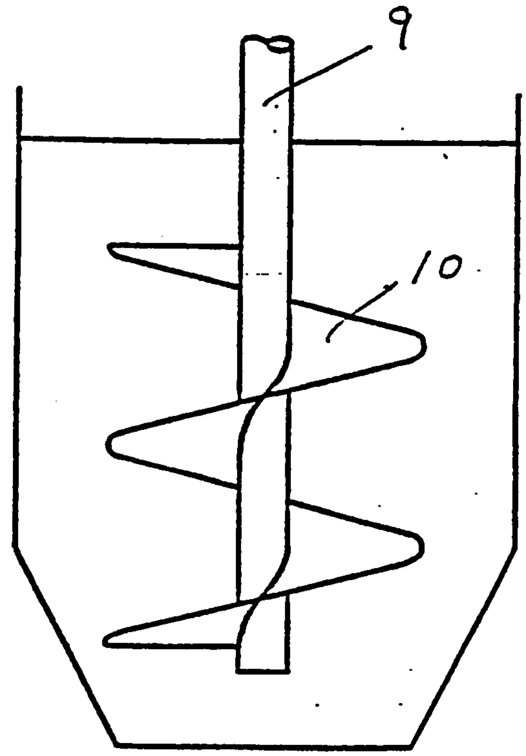



Fig 4b



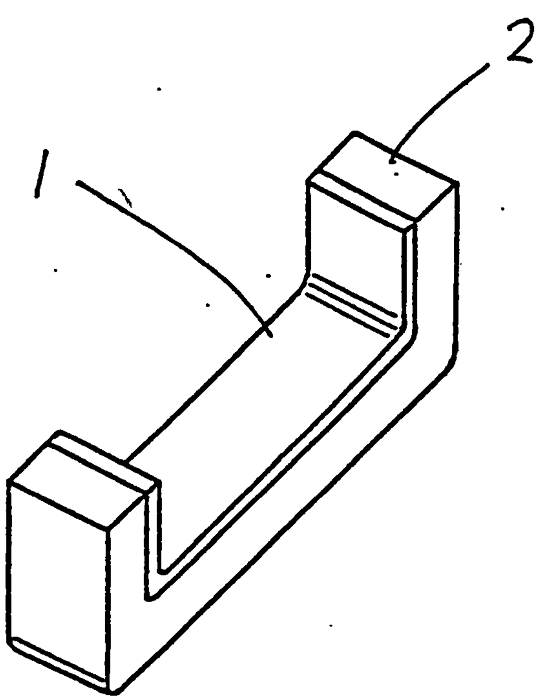




Fig 5a

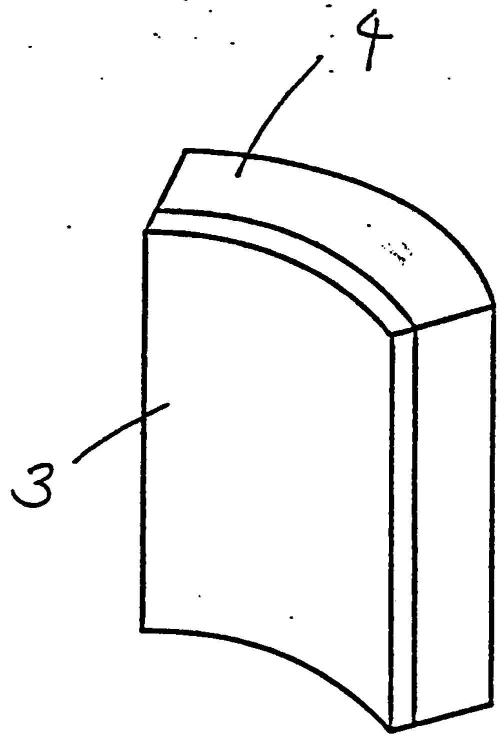



Fig 5 b

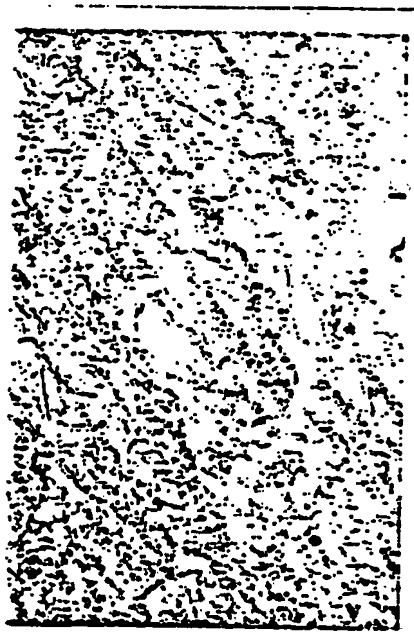


Fig 6 alloy No. 2

scale 0.1mm (X100)

Fig 7 alloy No. 8

scale 0.1mm (X100)

Fig 8 alloy No. 10

scale 0.1mm (X100)

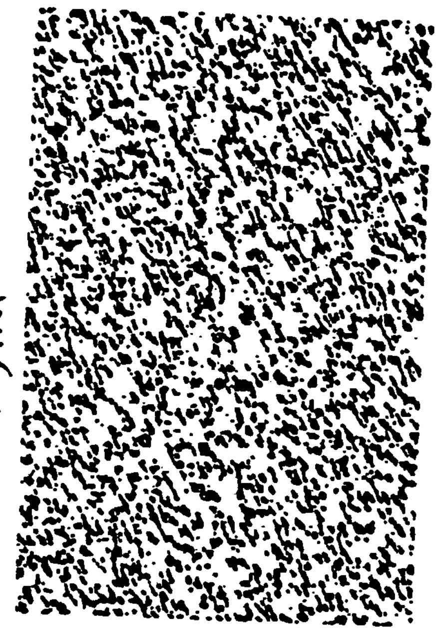


Fig 9 alloy No. 55

scale 0.1mm (X100)

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 88 11 2984

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
|---|---|---|---|
| X | SU-A- 450 844 (SVISTOUNOVA et al.)<br>* Whole document *<br>--- | 1 | C 22 C 19/05 |
| X | GB-A-1 383 995 (INTERNATIONAL NICKEL LTD)<br>* Claim 1; page 3, table I * & FR-A-2 168 402<br>--- | 1 | |
| X | US-A-2 809 139 (BLOOM et al.)<br>* Table II, line 10, "alloy composition 49 Cr, 49 Ni, 2 Mo"; column 6, line 62 - column 7, line 18 *<br>--- | 1 | |
| X | GB-A-1 470 911 (VSESOJUZNY NAUCHNO-ISSLEDOVATELSKY I PROEKTNY INSTITUT TEKNOLOGHII KHIMICHESKOGO I NEFTYANOGO APPARATO-STROENIA)<br>* Claims 1,2,6 *<br>--- | 1,7 | |
| A | GB-A-1 532 851 (ACIERIES DU MANOIR POMPEY)<br>* Claims 1-3 *<br>--- | | **TECHNICAL FIELDS SEARCHED (Int. Cl.4)** |
| A | GB-A- 459 848 (W.T. GRIFFITHS et al."Complete specification; page 3, lines 95-106,50-53; claims 1,7)<br>--- | 1 | C 22 C 19/05 |
| A | GB-A- 451 601 (HERAEUS-VACUUMSCHMELZE AG)<br>* Claims 1,2; page 1, lines 61-69 *<br>----- | 1 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 22-11-1988 | LIPPENS M.H. |

**CATEGORY OF CITED DOCUMENTS**

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document